

Diffuse Interstellar Bands in (Proto-) Fullerene-Rich Environments

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Abstract. The recent infrared detection of fullerenes (C₆₀ and C₇₀) in Planetary Nebulae (PNe) and R Coronae Borealis (RCB) stars offers a beautiful opportunity for studying the diffuse interstellar bands (DIBs) in sources where fullerenes are abundant. Here we present for the first time a detailed inspection of the optical spectra of the hot RCB star DY Cen and two fullerene PNe (Tc 1 and M 1-20), which permits us to directly explore the fullerenes - DIB connection. The DIB spectrum of DY Cen (García-Hernández *et al.* 2012a) is remarkably different from that in fullerene PNe (García-Hernández & Díaz-Luis 2013). In particular, Tc 1 displays unusually strong 4428 Å and 6309 Å DIBs, which are normal (or not seen) in DY Cen. On the other hand, DY Cen displays an unusually strong 6284 Å DIB that is found to be normal in fullerene PNe. We also report the detection of new broad and unidentified features centered at 4000 Å and 6525 Å in DY Cen and Tc 1, respectively. We suggest that the new 4000 Å band seen in DY Cen may be related to the circumstellar proto-fullerenes seen at infrared wavelengths (García-Hernández *et al.* 2012a). However, the intense 4428 Å DIB (probably also the 6309 Å DIB and the new 6525 Å band) may be related to the presence of larger fullerenes (e.g., C₈₀, C₂₄₀, C₃₂₀, and C₅₄₀) and buckyonions (multishell fullerenes such as C₆₀@C₂₄₀ and C₆₀@C₂₄₀@C₅₄₀) in the circumstellar envelope of Tc 1 (García-Hernández & Díaz-Luis 2013).

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1. Fullerenes in RCB stars and PNe

Fullerenes (e.g., C₆₀, C₇₀) are very stable molecules that are very important for interstellar/circumstellar chemistry and that may explain many astrophysical phenomena such as the mysterious diffuse interstellar bands (DIBs) and the intense UV bump at 2170 Å (e.g., Iglesias-Groth 2007; Cataldo & Iglesias-Groth 2009). Fullerenes were discovered in the laboratory (Kroto *et al.* 1985) and they have been found on Earth and on meteorites. Indeed, the 9577 and 9632 Å DIBs observed in some reddened stars lie near two electronic transitions of C₆₀⁺ (Foing & Ehrenfreund 1994; see also Berné *et al.* 2013 for a recent IR detection of the C₆₀ cation). At laboratory, fullerenes are efficiently produced under H-poor conditions (e.g., Kroto *et al.* 1985) and the so-called R Coronae Borealis (RCB) stars (extremely H-deficient stars) were thus expected to efficiently produce fullerenes (Goeres & Sedlmayr 1992). In 2010, García-Hernández, Rao & Lambert looked for C₆₀ in a complete sample of about 30 RCBs by using the Spitzer Space Telescope. We got the unexpected result that C₆₀-like mid-IR features were only detected in those RCBs with some H (García-Hernández *et al.* 2011a). In particular, C₆₀-like emission features were detected in the least H-deficient RCBs DY Cen and V854 Cen, which also show strong polycyclic aromatic hydrocarbon (PAH) features. Because of the unexpected result in RCBs, then we looked for fullerenes in ~240 Planetary Nebulae (PNe) by using data from our own Spitzer projects; five clear fullerene detections were found. Meanwhile,

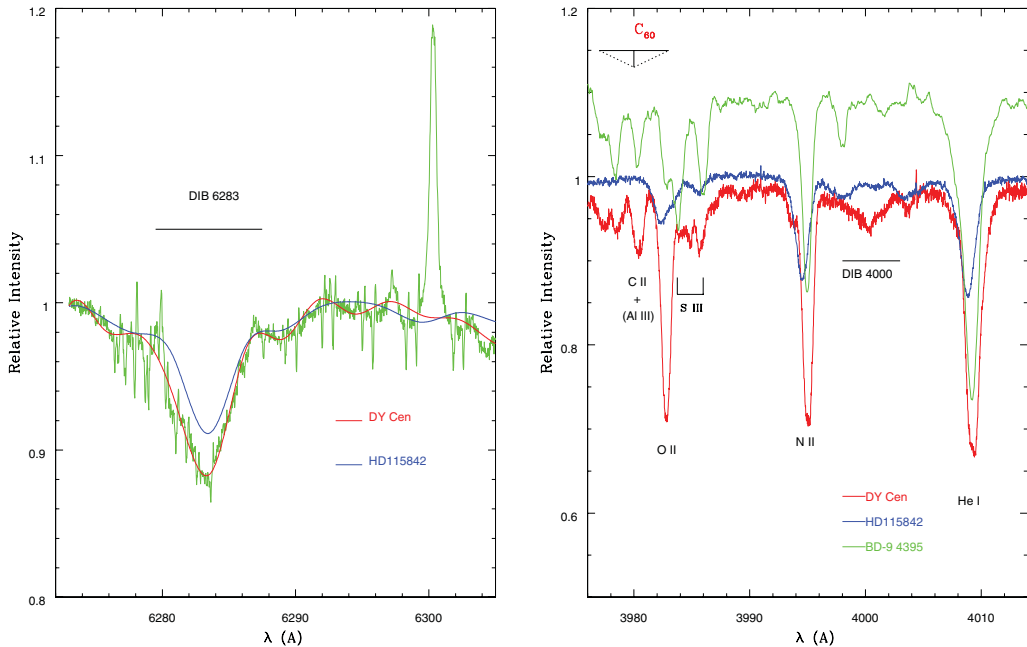


Figure 1. Left panel: Spectral region around the 6284 Å DIB in DY Cen (in red) and HD 115842 (in blue). The telluric line corrected spectrum of both stars are shown by smooth lines (red and blue). The non telluric corrected spectrum in DY Cen is also shown (in green). Right panel: The spectra of DY Cen (in red) and HD 115842 (in blue) around and 4000 Å where the extreme He star BD -9° 4395 is also displayed (in green). The expected position and FWHM of the C₆₀ feature at 3980 Å are marked on top of the spectra; there is no evidence (additional absorption) in DY Cen for the presence of this neutral C₆₀ feature. However, there is an additional absorption band at 4000 Å in DY Cen, which is not present in HD 115842 neither in BD -9° 4395.

Cami *et al.* (2010) reported the extraordinary discovery of the first IR detection of C₆₀ and C₇₀ fullerenes in the young PN Tc 1. At the same time, García-Hernández *et al.* (2010) confirmed the surprising results obtained in RCBs, showing that all PNe with fullerenes (including Tc 1) are low-mass C-rich PNe with normal H abundances. Contrary to the RCB stars, the Spitzer PNe spectra display C₆₀-like features in conjunction with very weak PAHs. This challenged our understanding of the fullerenes formation in space, showing that, contrary to general expectation, fullerenes are efficiently formed in H-rich circumstellar environments only. Furthermore, the detection of fullerenes in RCB stars and PNe suggests that large fullerenes may be formed as decomposition products of hydrogenated amorphous carbon (HAC) dust (García-Hernández *et al.* 2010, 2011a,b, 2012b; Bernard-Salas *et al.* 2012; Micelotta *et al.* 2012).

Thus, fullerenes and related large C-based molecules (e.g., other fullerenes as stable exohedral or endohedral metallo-complexes) might be ubiquitous in the interstellar medium and continue to be serious candidates for the DIB carriers. A detailed analysis of the DIBs towards fullerene-containing - accompanied or not by PAH molecules - space environments is very useful to learn about the nature of the DIB carriers. In this context, the recent detections of large fullerene-like molecules in RCBs and PNe offer a beautiful opportunity for studying the DIB spectrum of sources where fullerenes and fullerene-related molecules are abundant. Here we present for the first time a detailed inspection of the optical spectra of the hot RCB star DY Cen and two fullerene PNe (Tc 1 and M 1-20), which permits us to directly explore the fullerenes - DIB connection.

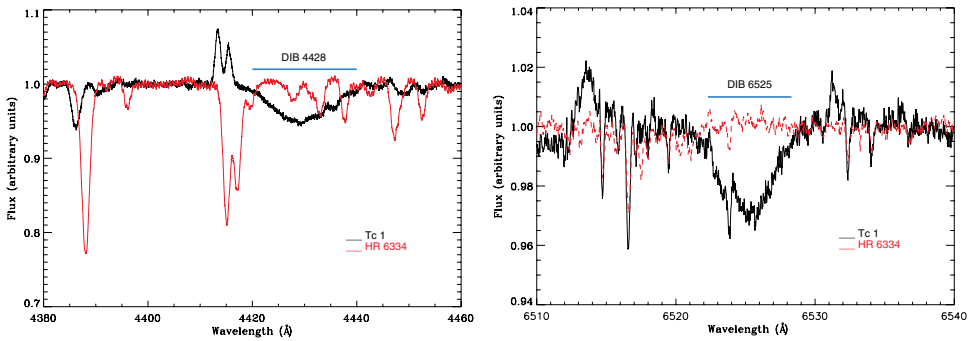


Figure 2. Left panel: Spectra of Tc 1 (in black) and HR 6334 (in red) around the 4428 Å DIB. This DIB is found to be unusually strong in Tc 1 while HR 6334 - with a higher $E(B-V)$ of 0.42 - does not show evidence of its presence. Right panel: Spectral region around the new broad unidentified band at 6525 Å in Tc 1 (in black) and HR 6334 (in red).

2. Our DIB survey

We acquired high-resolution ($R \geq 15,000$) and high signal-to-noise ($S/N \geq 200$) VLT-UVES optical ($\sim 3300\text{-}9450$ Å) spectra of the RCB star DY Cen and PN Tc 1. The PN M 1-20 was also observed although at lower S/N . Nearby B-type comparison stars were observed on the same dates as the corresponding science objects using the same VLT-UVES set-up. The observational details are not repeated here and we refer the reader to García-Hernández *et al.* (2012a) and García-Hernández & Díaz-Luis (2013) for the observations of DY Cen and Tc 1 (and M 1-20), respectively. The Spitzer IR spectrum of DY Cen is dominated by PAH-like features with weaker C_{60} -like features (García-Hernández *et al.* 2011a) while Tc 1 displays a C_{60} -dominated IR spectrum with very weak (or absent) PAH bands (Cami *et al.* 2010; García-Hernández *et al.* 2010). The goal of our optical observations is to study the characteristics of DIBs in fullerene-containing environments as well as to shed some light about the possible fullerenes - DIB connection.

We find that the classical and well-studied DIBs (e.g., those at 4428, 5780, 5797, 5850, 6196, 6379, and 6614 Å) towards DY Cen are normal for its reddening. The only exception is the DIB at 6284 Å (possibly also the 7223 Å DIB) (see García-Hernández *et al.* 2012a for more details). Figure 1 (left panel) shows the region of 6284 Å for DY Cen and the nearby comparison star HD 115824. It is clear that this DIB towards DY Cen is stronger than towards HD 115842, suggesting that the carrier of the 6284 Å DIB (along with 7223 Å) is different from the rest of the classical DIBs. Also interesting is that we detect in DY Cen a broad (FWHM ~ 2 Å) unidentified feature centered at ~ 4000 Å, which is seen in DY Cen only (Fig. 1; right panel). Note that no DIBs are known at this wavelength (see e.g., Hobbs *et al.* 2008) and no molecule is known to exhibit a strong electronic transition at ~ 4000 Å. In addition, García-Hernández *et al.* (2012a) have reported the non-detection of the strongest C_{60} electronic transitions (e.g., those at ~ 3760 , 3980, and 4024 Å) in DY Cen (see Fig. 1, right panel); C_{60} IR column density estimates are 1000 times higher than the optical detection limits.

Similarly to DY Cen, we find the strongest DIBs (e.g., those at 5780, 5797, 5850, 6196, 6270, 6284, 6380, and 6614 Å) most commonly found in the ISM to be normal in Tc 1 and M 1-20 (see García-Hernández & Díaz-Luis 2013 for more details). This may suggest that the carriers of the latter well-studied DIBs are not particularly overabundant in fullerene PNe. Surprisingly, the well-studied DIB at 4428 Å as well as the weaker 6309 Å DIB (see e.g., Hobbs *et al.* 2008) are found to be unusually strong towards Tc 1; the 4428 Å DIB is unusually strong in M 1-20 too. Figure 2 (left panel) compares the

Table 1. Overview of DIBs in fullerene-containing RCBs and PNe.

DIB	RCBs (DY Cen)	PNe (Tc 1)
4000 Å	yes	no
4428 Å	normal	strong
6284 Å	strong	normal
6309 Å	no	yes
6525 Å	no	yes

4428 Å DIB in Tc 1 with that in the nearby comparison star HR 6334. Adopting a Lorentzian profile for the 4428 Å DIB, we obtain an EQW of 860 mÅ, which is at least a factor of two greater than expected from the reddening in Tc 1. An unidentified broad (FWHM ~ 5 Å) feature at 6525 Å is also detected in Tc 1[†]. Figure 2 (right panel) displays the unidentified 6525 Å band in the Tc 1 spectrum in comparison with the star HR 6334. Again, the most intense optical bands of neutral C₆₀ are lacking in the Tc 1 spectrum; although this could be explained by the low C₆₀ column density estimated from the C₆₀ IR features if the neutral C₆₀ emission peaks far away from the central star (García-Hernández & Díaz-Luis 2013). Finally, the DY Cen's unidentified 4000 Å band is not seen in Tc 1.

3. Diffuse interstellar bands in (proto-) fullerene-rich environments

Table 1 compares the DIBs seen in the RCB star DY Cen with those in the fullerene PN Tc 1. This table naturally prompts the question of why DIBs are so different in the fullerene-containing environments around RCB stars and PNe?

Based on their laboratory spectroscopy of HAC nanoparticles, Duley & Hu (2012) propose that the C₆₀ IR features seen in sources with PAH-like dominated IR spectra such as DY Cen are attributable to proto-fullerenes or fullerene precursors rather than to C₆₀. Our non-detection of neutral C₆₀ in the DY Cen optical spectrum may support the Duley & Hu (2012) HAC laboratory results. Thus, the new 4000Å band seen in DY Cen may be related to the circumstellar proto-fullerenes; perhaps an organic compound containing pentagonal rings. These pentagonal carbon rings are usually present in HAC nanoparticles and nanotubes, suggesting that they may be intimately related with the formation process of fullerenes. In addition, the 4428 Å DIB has been linked to fullerenes bigger than C₆₀ and/or buckyonions such as C₆₀@C₂₄₀ and C₆₀@C₂₄₀@C₅₄₀ (Iglesias-Groth 2007). Our findings in DY Cen would be consistent with fullerenes and fullerene-containing molecules not being especially overabundant towards DY Cen.

On the other hand, the non detection of neutral C₆₀ in the Tc 1 optical spectrum is intriguing. Tc 1 - with no or very weak PAHs - is expected to be rich in C₆₀ (Duley & Hu 2012). An exotic explanation may be that larger fullerenes or more complex fullerene-based molecules are present. This is suggested by the unusually strong 4428Å DIB. Photo-absorption theoretical models of large fullerenes (C₈₀, C₂₄₀, C₅₄₀) and buckyonions (C₆₀@C₂₄₀, C₆₀@C₂₄₀@C₅₄₀) (Iglesias-Groth 2007) display strong transitions around 4428 Å. In this framework, the 4428Å DIB may be explained by the transitions (superposition) of fullerenes bigger than C₆₀ and multishell fullerenes (buckyonions) (Iglesias-Groth 2007). Recent studies of the 4428Å DIB also suggest the carrier to be a resistant, large and compact neutral molecule (van Loon *et al.* 2013).

[†] A few other unidentified bands and/or unusually strong DIBs seem to be present in Tc 1 (see Machado *et al.* these proceedings).

4. Concluding remarks

The IR detection of C₆₀ in RCB stars and PNe offers the opportunity of studying DIBs in environments where fullerenes are abundant. We have shown here that DIBs in RCB stars and PNe are remarkably different. The new 4000 Å band detected in the RCB star DY Cen is suggested to be related with proto-fullerenes or fullerene-precursors (García-Hernández *et al.* 2012a). However, the unusually strong 4428 Å DIB (probably also the weaker 6309 Å DIB and the unidentified 6525 Å band) in PNe is suggested to be related with the presence of large fullerenes and buckyonions (García-Hernández & Díaz-Luis 2013) as previously pointed out by Iglesias-Groth (2007) from theoretical considerations.

At present, the HAC's photochemical processing seems to be the most promising C₆₀ formation route; at least in the complex circumstellar envelopes of RCB stars and PNe (see e.g., García-Hernández *et al.* 2012b; and references therein) but see also Berné & Tielens (2012). Larger fullerenes and fullerene-based molecules may form from pre-existing C₆₀ molecules (e.g., Dunk *et al.* 2012), opening the possibility of forming a rich family of fullerene-related molecules such as buckyonions, metallofullerenes, and fullerene adducts. These complex fullerene-based molecules may emit through the same IR vibrational modes (e.g., as isolated C₆₀ and C₇₀), being indistinguishable from C₆₀ (and C₇₀) on the basis of IR spectra alone. In particular, fullerenes and PAHs may be mixed in the circumstellar envelopes of fullerene PNe (e.g., M 1-20) and fullerene/PAH adducts may form via Dier-Alder cycloaddition reactions (García-Hernández *et al.* 2013). Indeed, very recent laboratory work demonstrates that fullerene/PAH adducts - such as C₆₀/anthracene Dier-Alder adducts - display mid-IR features strikingly coincident with those from C₆₀ and C₇₀ (García-Hernández *et al.* 2013).

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